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GEOCHEMICAL STUDY OF AN EQUINE ENTEROLITH, MEDINA COUNTY, OHIO[1]

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ABSTRACT. An intestinal concretion (enterolith) was recovered during necropsy of a horse from Medina County, Ohio. The object is approximately spherical in shape and measures 9 × 8 × 7 cm in diameter. It is composed of struvite ($NH_4MgPO_4 \cdot 6H_2O$). The monohydrate dittmarite was not found. In addition to Mg and P, significant concentrations (≥500 ppm) of Ca, K, and Fe and lesser amounts (≤500 ppm) of Na, Mn, Rb and Sr were measured. The concretion is concentrically zoned with concentrations of Ca, Sr, Fe and Na decreasing from the inside out whereas those of K and Rb increase. The concentrations of Mg and Mn appear to be constant within analytical uncertainty. The cause for the chemical zonation of the enterolith is not known. The Rb/Sr ratio of the struvite is high compared to that of calcium phosphate and ranges from 4.9 to 20.7. The $^{87}Sr/^{86}Sr$ ratio is 0.7101 ± 0.0003 which leads to the interpretation that most of the Sr available to plants in the soil of Medina County was derived from particles of Devonian limestone ($^{87}Sr/^{86}Sr = 0.7083$) and lesser amounts from feldspar ($^{87}Sr/^{86}Sr = 0.7141$) and clay ($^{87}Sr/^{86}Sr = 0.7345$).

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INTRODUCTION

Intestinal concretions called enteroliths are frequently found in horses but only rarely in other animals. They occur in the stomach-like dilatation of the large colon either singly or in clusters and are usually spherical in shape. They range from pea-size to objects weighing up to 11 kg (Blue and Wittkopp 1981). Most enteroliths are composed of struvite ($NH_4MgPO_4 \cdot 6H_2O$) and may contain fragments of undigested food, hair and mucus. In addition, several chemical elements including Ca, Na, K and Fe as well as carbonate and chloride ions have been reported. (Nieberle and Cohrs 1967).

Equine enteroliths form by precipitation of insoluble chemical compounds around a foreign object in the colon, but the specific causes for their formation are not known.

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Blue and Wittkopp (1981) reported the presence of small chert pebbles in the centers of equine enteroliths recovered during necropsy or laparotomy from 11 horses near Davis, CA. Additional enteroliths were found in pastures where they had been excreted by clinically healthy horses. They identified both monohydrate and hexahydrate forms of NH_4MgPO_4 in X-ray diffraction patterns of concentric layers within several enteroliths. They also reported that the chemical composition of an enterolith removed from the small colon of a 7-year-old Arabian stallion consisted mainly of Mg (12%) and P (18%) with lesser amounts of Ca (0.18%), Mn (375 ppm), Fe (25 ppm), Zn (9 ppm), Cu (8.5 ppm), and Ni (2 ppm). The drinking water from the farm on which the Arabian stallion was raised was found to contain an unusually high concentration of Mg^{+2} (53 ppm) compared to Ca^{+2} (25 ppm), Na^{+} (23 ppm) and K^{+} (8 ppm). A similar composition of water was observed near Davis, CA, where equine enteroliths are found with abnormal frequency (Blue and Wittkopp 1981). A summary of 30 case histories of equine enteroliths was published by Blue (1979), and a general review of the occurrence of minerals in the plant and animal kingdoms was presented by Lowenstam (1981).

The objective of this study was to determine whether the chemical composition of an equine enterolith varies systematically as a function of distance from the center, thereby presumably recording changes in the composition of the intestinal fluid.

METHODS AND MATERIALS

We analyzed an enterolith recovered during necropsy of a horse from Medina County, Ohio. The enterolith (fig. 1) is approximately spherical in shape with 3 flattened faces suggesting it may have been part of a cluster of 4 stones. It is approximately 9 × 8 × 7 cm in diameter and has a density of 1.72 g/cm^3. The surface has a tan to light brown color that changes to bluish gray after drying and exposure to air. A slice, approximately 10 mm thick, was sawed from the center of the enterolith and was divided into 3 samples shown as A (inner), B and C (outer) in fig. 1.

The center of this enterolith contains a fragment of metallic iron that was identified by X-ray fluorescence. The mineral matter occurs in concentric layers about this nucleus and consists both of thin laminations and radiating crystals. Fragments of undigested food (hay or straw?) and horse hair occur in the central region around the iron nucleus. The zones composed of radiating crystals appear to be porous and contain fragments of organic matter whereas the laminated portions are cryptocrystalline and dense. The laminations are marked by dark-colored bands and average about 0.5 mm in width.

Concentrations of Mg and Ca were determined by atomic absorption spectrometry, Na and K by flame emission spectrometry, and Sr, Rb, Fe and Mn were measured by X-ray fluorescence spectrometry. Calibrations for Mg, Ca, Na, and K were based on standard solutions whereas the determinations of Sr, Rb, Fe and Mn were obtained by comparison with rock standards of the U.S. Geological Survey (Flanagan 1973). The isotopic composition of Sr, expressed by the $^{87}Sr/^{86}Sr$ ratio, was measured by standard methods using a solid-source mass spectrometer (Faure and Powell 1972, Faure 1977). The Eimer and Amend $SrCO_3$ isotope standard was analyzed in duplicate and yielded an average $^{87}Sr/^{86}Sr$ ratio of 0.7081 ± 0.0002. This value is in agreement with results obtained by other analysts.

RESULTS

MINERAL COMPOSITION. X-ray diffraction patterns of each of the 3 portions of the enterolith are identical and indicate it is composed of the mineral struvite ($NH_4MgPO_4 \cdot 6H_2O$). The d-spacing, calculated from 2θ values of the principal diffraction peaks, (table 1) match all of the diffraction peaks for this mineral on file card 15-762

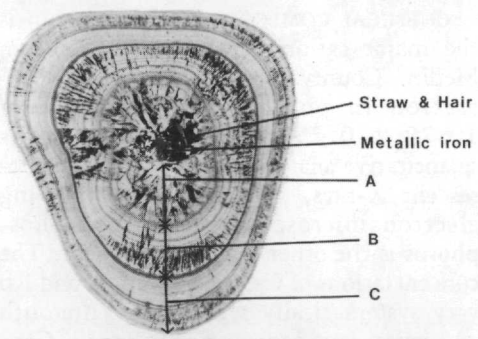

FIGURE 1. Photograph of an enterolith removed from the intestine of a horse from Medina County, Ohio. A 10-mm thick slice of the enterolith was subdivided into samples A, B and C as shown.

TABLE 1.

Listing of d-spacing and relative intensities of X-ray diffraction peaks of struvite ($NH_4MgPO_4 \cdot 6H_2O$) obtained for an enterolith from a horse in Medina County, Ohio.

d(Å)	I %	d(Å)	I %
5.60_4	100	2.66_4	26
4.26_6	83	5.94_0	22
4.14_8	74	2.96_6	17
2.69_2	72	6.14_5	16
2.80_2	54	1.79_9	14
4.40_0	43	2.01_7	11
3.29_9	28	1.96_1	11
2.91_9	26	4.61_8	7

of the American Society for Testing and Materials. Struvite crystallizes in the orthorhombic system, has a hardness of 2 on the Mohs Scale, and a specific gravity of 1.711. It occurs in deposits of guano and dung, spoiled food, and may be formed by bacterial action in various organic compounds (Palache et al. 1951). It has also been reported in human bladder and kidney stones (Frondel and Prien 1947) and with newberyite ($HMgPo_4 \cdot 3H_2O$) in the tooth of a mammoth from Quartz Creek near Dawson, Yukon Territory, Canada (Hoffmann 1901). The enterolith we studied does not contain the monohydrate dittmarite ($NH_4MgPO_4 \cdot H_2O$, A.S.T.M. file card 20-663) that was found by Blue and Wittkopp (1981) in equine enteroliths from California.

CHEMICAL COMPOSITION. Magnesium is the major cation in the enterolith from Medina County with an average concentration in portions A, B and C of 10.78 ± 0.25% (table 2). A semiquantitative analysis by dispersion of fluorescent X-rays, generated in a scanning electron microscope, confirmed phosphorus is the other major component. The concentrations of Ca, Sr, Fe, Na, K and Rb vary systematically within the enterolith and reveal it is concentrically zoned. Concentrations of Ca, Sr, Fe and Na decrease outward within the enterolith whereas those of K and Rb increase. Concentrations of Mn and Mg appear to remain constant within the range of analytical uncertainty (figure 2).

ISOTOPE COMPOSITION OF STRONTIUM. The isotopic abundance of ^{87}Sr in rocks and minerals increases as a function of time because of the decay of naturally occurring ^{87}Rb to stable ^{87}Sr with a half-life of 48.8×10^9 years (Faure and Powell 1972, Faure 1977). The isotopic composition of a particular sample of Sr is conventionally expressed by the $^{87}Sr/^{86}Sr$ ratio which reflects both the age of the rock or mineral in which it resides and its previous history. The $^{87}Sr/^{86}Sr$ ratio of portion A of the enterolith from Medina County is 0.7101 ± 0.0003.

DISCUSSION

The abundances of the alkali metals (Na, K, and Rb) are surprisingly high because Ca and Mg phosphates are usually depleted in alkali metals. We propose the ions of the alkali metals enter the crystal lattice of struvite by replacement of NH_4^+ because their ionic radii are similar (K^+ = 1.33Å, Rb^+ = 1.49Å, NH_4^+ = 1.43Å). However, the radius of Na^+ (0.98Å) is significantly smaller than that of NH_4^+ which is unfavorable for substition and probably accounts for the low concentration of Na compared to K. The ionic radii of Fe^{+2} (0.75Å) and Mn^{+2} (0.80Å) are similar to that of Mg^{+2} (0.65Å). Therefore substitution among these ions is common and accounts for the presence of the 2 elements in the enterolith.

The presence of Ca^{+2} (0.99Å) and Sr^{+2} (1.13Å) in the enterolith is not readily accounted for by replacement of Mg^{+2} (0.65Å) because these 2 ions are too large to permit extensive substitution of Mg^{+2}. Instead, Ca may form a separate phase such as collophane ($Ca_3(PO_4)_2 \cdot H_2O$) found in coral limestone covered by beds of guano (Ford 1954), or it may occur in another compound, such as $NH_4CaPO_4 \cdot H_2O$ (A.S.T.M. file card 20-202). However, a search of the X-ray diffraction pattern of the enterolith did not confirm the presence of this compound. In fact if Ca is present

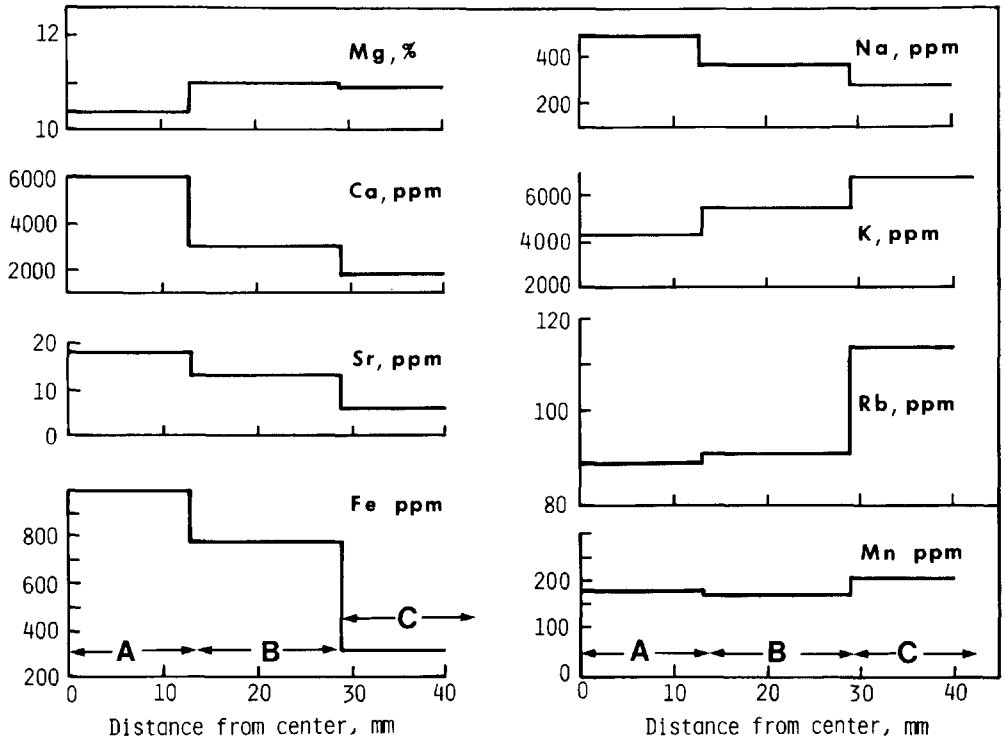

FIGURE 2. Concentric variation of the chemical composition of the enterolith.

as $NH_4CaPO_4 \cdot H_2O$, its abundance in the struvite of portion A of the enterolith (Ca = 0.59%) would be about 2.5% which is too low for detection by X-ray diffraction. The Sr concentration of the enterolith is quite low (5.47 to 18.12 ppm) compared to that of Ca. The failure of Sr^{+2} to replace Ca^{+2} more extensively suggests Ca^{+2} occupies a lattice site having 6-fold coordination that discriminates against Sr^{+2} which prefers sites with 8-fold coordination (Mason 1958).

The concentric variation of the chemical composition of equine enteroliths has not been reported previously as far as we know and may convey significant information about changes in the chemical composition of the body fluid from which the struvite concretion precipitated as it grew in the intestine of its host. The evidence in table 2 indicates the body fluid became depleted in Ca, Sr, Fe and Na whereas concentrations of K and Rb increased. The causes for these chemical changes are not known, but may include both changes in the composition of feed or water of the animal and a deterioration of its health. If the chemical zonation of the enterolith was caused by change in the composition of feed related to the seasons, then the growth period of the concretion may be one year or less. Nieberle and Cohrs (1967) stated the rate of growth of enteroliths was unknown but reported 2 cases in which an intestinal calculus 15 cm in diameter had formed in 2 years and one of "fist-size" had grown in one year. Therefore the enterolith from Medina County (9 × 8 × 7 cm) could have formed in one year.

The Rb/Sr ratio of the enterolith varies concentrically from 4.9 (portion A) to 20.7 (portion C) because the concentration of Rb increases from the inside out whereas Sr decreases (table 2). The value of this ratio

TABLE 2.

Analytical data for an enterolith of a horse, Medina County, Ohio.

	A interior	B intermediate	C exterior
Interval, mm	0-13	13-29	29-42
Mg, %	10.37	11.05	10.91
Ca, ppm	5901	2975	1759
Na, ppm	489	361	266
K, ppm	4388	5467	6712
Fe, ppm	995 ± 21	775 ± 21	310 ± 99
Mn, ppm	182 ± 44	173 ± 30	211 ± 55
Rb, ppm	88.9 ± 1.5	90.7 ± 1.2	113.7 ± 2.6
Sr, ppm	18.12 ± 0.06	13.22 ± 0.06	5.47 ± 0.32
$^{87}Sr/^{86}Sr$	0.7101 ± 0.0003	—	—

is remarkably high compared to those commonly observed in other phosphate minerals that occur in igneous, sedimentary, and metamorphic rocks. The average Sr content of 58 apatites ($Ca_5(PO_4)_3(OH,F)$) from igneous and metamorphic rocks is 1943 ppm (Stueber 1978). The Rb concentration of apatite is less than 0.1 ppm and is rarely measured. Therefore, the high and variable Rb/Sr ratio of struvite concretions may permit them to be dated by the Rb-Sr method, if such concretions are found in geologic rock formations (Faure 1977). None have been found as far as we know.

In order to interpret the $^{87}Sr/^{86}Sr$ ratio of the enterolith, we first review some aspects of the geology of Medina County. The bedrock consists primarily of shale, sandstone and limestone of the Waverly and Maxville Formations of Mississippian age (fig. 3). These are overlain by scattered outliers of the Pottsville and Allegheny Formations of early Pennsylvanian age composed of coal, sandstone, shale and limestone (Bownocker 1947). These rocks are covered by ground and recessional moraines of late Wisconsin age (Goldthwait et al. 1961). The glacial deposits were derived primarily from areas north of Medina County and were deposited by the Erie lobe of the last Laurentide ice sheet that retreated from Ohio about 14,000 years ago.

The isotopic composition of Sr entering the struvite concretion in the intestine of the horse depends on the Sr in its feed and water, and those depend on the isotopic composition of Sr in the soil of Medina County. The principal Sr–bearing minerals in the soils of northern Ohio are calcite ($CaCO_3$) derived from outcrops of Devonian limestone along the shore and within the basin of Lake Erie, feldspar (K, Na and Ca silicates) from the Precambrian Shield of Canada, and clay minerals from Paleozoic shales and lacustrine clays of Lake Erie. All 3 minerals contribute Sr to plants and to

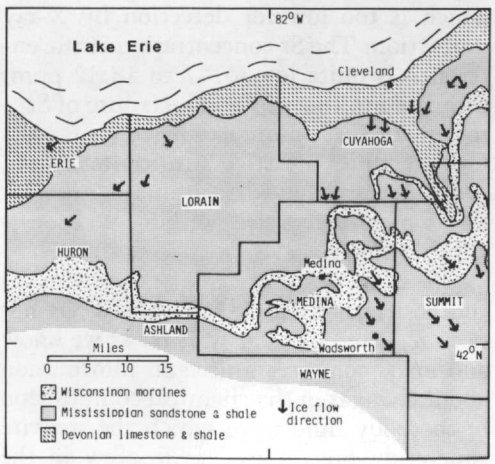

FIGURE 3. Geologic map of Medina and neighboring counties in Ohio. (After Bownocker 1947, Goldthwait et al. 1961.)

groundwater in varying proportions that depend on the concentrations of Sr and the solubility of the respective minerals. The $^{87}Sr/^{86}Sr$ ratio of Sr in plants and water are therefore a composite of the isotopic composition of Sr in the 3 principal sources in the soil. According to a recent compilation of data from the literature by Faure (1982), the $^{87}Sr/^{86}Sr$ ratio of Devonian limestones is 0.7083 ± 0.0003. Measurements of $^{87}Sr/^{86}Sr$ ratios in 19 feldspars from till in the Powell-Union City Moraine of Ohio by Taylor and Faure (1981) yielded an average value of 0.7141 ± 0.0003. The clay and silt-size fractions of this till contain Sr with an average $^{87}Sr/^{86}Sr$ ratio of 0.7345 ± 0.0012 (Taylor and Faure 1979). A comparison of these $^{87}Sr/^{86}Sr$ ratios to that found in the Medina enterolith (0.7101) indicates calcite particles are probably the dominant source of nutrient-Sr in the soils of Medina County.

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